

USE OF DIALKYL CARBONATES AS SOLVENTS FOR EXPANDED POLYSTYRENE

The present invention relates to the use of dialkyl carbonates as solvents capable of reducing the volume of expanded polystyrene, and in particular to the use of dialkyl carbonates as solvents in a new method for the recycling of expanded polystyrene.

Expanded polystyrene is used in large quantities as a packaging material of various products and as a thermal insulation material for the building industry and refrigerators, as a result of its characteristics of low thermal conductivity and good shock absorbance capacity. The waste deriving from these materials and the production scraps of expanded polystyrene are extremely bulky, as their specific weight is very low, and consequently their transportation and disposal in dumps create various problems. The disposal of these waste materials by incineration is also a problem, as it can interfere in the combustion process of the incineration oven and can also produce toxic gases. Some types

of expanded polystyrene containing brominated flame-retardant additives, when incinerated, can in fact produce polybrominated dioxins, which are extremely toxic. For these reasons, the waste material from expanded polystyrene 5 should be recycled, after a first step of volume reduction, effected in the production or waste collection sites, followed by the regeneration of the polystyrene, carried out in a centralized recovery plant.

The traditional methods for reducing the volume and 10 the recycling of polystyrene, which envisage thermal treatment, do not allow the complete separation of polystyrene from the other products present in expanded polystyrene, and also have the great disadvantage of causing the partial oxidative degradation of the polymer, thus reducing its 15 quality (Kano, Suzuki, J. Jpn. Pack. Inst., 31, 33, 1993; Sasao, Harade et Al., Kagaku Kogyo, 66, 395, 1992).

Another volume reduction method of expanded polystyrene described in the known art, which overcomes the above described drawbacks, is to dissolve the polymer in an organic solvent. Organic solvents which can appropriately 20 dissolve polystyrene are aromatic hydrocarbons such as toluene and xylenes (U.S. Patent 4,031,039) and halogenated solvents, such as methylene chloride, perchloro ethylene (U.S. Patent 5,891,403). These solvents have the disadvantage 25 of being flammable or dangerous for human beings and

the environment. The use of solvents such as d-limonene has been proposed for overcoming these drawbacks (Noguchi, Miyashita, et al., Packag. Technol. Sci. 11, 19-27 (1998), which however has a strong smell of lemon and a low flash point (47°C); glycol alkyl ethers, some of which are harmful or even toxic, such as diethylene glycol dimethyl ether; dialkyl esters of organic acids, such as dimethyl adipate, dimethyl glutarate and dimethyl succinate (U.S. Patent 5,629,352). When the recovery of polystyrene from the solution is carried out by the evaporation of the solvent, the use of high boiling solvents, such as d-limonene, glycol dialkyl ethers and dialkyl esters of organic acids has the disadvantage of requiring, during the distillation phase of the solvent, very low pressures and the use of costly distillation equipment, in order to avoid the decomposition of polystyrene. In order to solve this problem, the recovery of polystyrene from the solution is effected, in U.S. Patent 5,629,352, by means of precipitation by the addition of water. These methods, as also those which envisage the recovery of polystyrene by evaporation of the organic solvent, have the disadvantage of not allowing the separation from polystyrene of the majority of additives present in the expanded polystyrene, such as, for example, brominated flame-retardant additives, which are soluble in said organic solvents and insoluble in water. In the patent

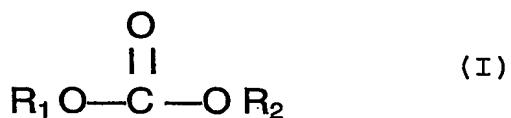
WO 0238659, the volume of the expanded polystyrene is reduced by treating it with a series of solvents consisting of a solvent capable of dissolving polystyrene, such as, for example, dialkyl esters of organic acids, and a non-  
5 solvent of the polymer, such as, for example, ethylene or propylene glycol and others. This treatment does not dissolve the expanded polystyrene but simply collapses it. The collapsed polystyrene, in gel form, is then separated and dried. Other methods similar to the previous one, which  
10 differ in the series of solvents and in the equipment used, are disclosed in patents WO 0222337, U.S. 2002/0120020. With these methods, the polystyrene, separated in gel form, withholds impurities and large amounts of solvent, which are difficult to remove during the drying phase.

15       The drawback of all these methods is that it is impossible to obtain pure polystyrene, without all the foreign components normally present in expanded polystyrene, such as labels, other polymers, additives and other materials. In patents EP 0894818 and WO 0214413, the recycling of the  
20 polymers in general with separation from foreign materials and additives is obtained by dissolving the polymeric material in a suitable solvent, by separating the insoluble components and recovering the desired polymer by precipitation with a non-solvent. These patents do not provide examples of the recycling of expanded polystyrene and the sol-

vents used for dissolving the polymeric material are, for the most part, flammable, toxic or harmful.

It has now been found that the drawbacks of the known art can be overcome if a dialkyl carbonate is used as solvent for dissolving expanded polystyrene.

In accordance with the above, an object of the present invention relates to the use of a dialkyl carbonate, or a blend of dialkyl carbonates, having general formula (I):



10

wherein  $\text{R}_1$  and  $\text{R}_2$ , the same or different, have the following meaning:

-  $\text{R}_1$ ,  $\text{R}_2$  represent linear, branched or cyclic alkyl radicals, containing from 1 to 12 carbon atoms, preferably linear or branched radicals containing from 1 to 8 carbon atoms.

- the sum of carbon atoms of  $\text{R}_1$  and  $\text{R}_2$  is between 2 and 15, preferably between 5 and 10.

as solvents for expanded polystyrene.

20 A further object of the present invention relates to a process for the recycling of expanded polystyrene, which is based on the use of dialkyl carbonates, having general formula (I), as solvents.

In particular, the process of the invention comprises:

25 (a) the reduction in volume of expanded polystyrene by

dissolution in a dialkyl carbonate or a blend of dialkyl carbonates having formula (I);

- (b) the removal of the insoluble components;
- (c) the selective precipitation of polystyrene with a non-solvent or a blend of non-solvents;
- 5 (d) the separation, drying and extrusion of the precipitated polystyrene.

Preferred dialkyl carbonates are those having a flash point higher than 55°C, such as, for example, di-n-butyl carbonate (flash point= 92°C), di-isobutyl carbonate (flash point = 84°C), di-n-propyl carbonate (flash point = 62°C).

Dialkyl carbonates, whose use is the object of the present invention, are thermally stable solvents, with a 15 particularly favorable toxicological and eco-toxicological profile, which allows their storage and application without any particular precautions. Dialkyl carbonates can be prepared by the transesterification of dimethyl carbonate with alcohols, using the known methods, as described, for example in Chem. Rev. 96, 951-976 20 (1996). Dimethyl carbonate can, in turn, be obtained by the oxidative carbonylation of methanol, as described in EP 460732.

Dialkyl carbonates are excellent solvents for expanded 25 polystyrene and their solvent capacity decreases with an

increase in the number of carbon atoms of the alkyl chains.

Low-boiling dialkyl carbonates, such as dimethyl carbonate (flash point = 17°C) and methyl ethyl carbonate, have a capacity of dissolving expanded polystyrene similar to that of the best solvents of the known art, such as methylene chloride, which is suspected to be cancerous; ethyl acetate, which has a lower flash point (-4°C); butyl acetate, which has a higher toxicity and eco-toxicity; and toluene, which is harmful. Dialkyl carbonates with a higher boiling point and flash point (over 55°C), such as, for example, di-n-propyl carbonate and di-n-butyl carbonate, have a solvent capacity with respect to polystyrene which is higher than that of alkyl di-esters of di-carboxylic acids, such as dimethyl succinate and dimethyl adipate and similar to that of limonene and di-ethylene glycol di-methyl ether, which is toxic.

The dissolution of expanded polystyrene with dialkyl carbonate is effected at atmospheric pressure, in an apparatus preferably equipped with a stirring system, at a temperature ranging from 20°C to 70°C, preferably room temperature.

The polystyrene concentration in the solution is between 5% and 50% by weight, preferably within the range of

15% to 40% by weight.

The insoluble components, possibly present, are separated from the polystyrene solution in the dialkyl carbonate or the blend of dialkyl carbonates, through conventional solid/liquid separation procedures, such as, for example, decanting, filtration and centrifugation.

The selective recovery of polystyrene from the solution is effected by treatment with a non aqueous solvent, or blend of solvents, which are preferably miscible with dialkyl carbonate, characterized by being non-solvents for polystyrene and good solvents for the additives. Following this treatment, the polystyrene precipitates and the additives remain in solution.

Examples of solvents which can be used for the selective precipitation of polystyrene, are:

glycols, such as ethylene and propylene glycol; alcohols, such as n-butyl and iso-propyl alcohol; alkylene carbonates such as propylene carbonate, ethylene carbonate, butylene carbonate; dialkyl carbonates with a number of carbon atoms equal to or higher than 17, such as di-iso-octyl carbonate; alkyl esters of fatty acids.

Examples of additives which can be separated from the expanded polystyrene are brominated flame-retardant additives, such as for example hexabromocyclododecane (HBCD); coadjuvants of flame-retardant additives, such as for exam-

ple dicumyl peroxide (DCP). These additives must be removed from the expanded polystyrene to avoid the formation of toxic gases, the degradation and colouring of the polymer during the subsequent extrusion phase.

5       The precipitation of the polystyrene is carried out at a temperature ranging from 10°C to 70°C, preferably within the range of 15°C to 60°C, by feeding the polystyrene solution to the non-solvent, maintained under turbulent stirring.

10      The quantity of non-solvent (or blend of non-solvents) used is in a weight ratio with the dialkyl carbonate ranging from 2:1 to 20:1, preferably within the range of 3:1 to 15:1.

15      The feeding of the polystyrene solution is effected on the bottom of the precipitation reactor, below the stirring system, with a flow-rate, expressed in g/(hour\*litre of non-solvent), within the range of 30-1500, preferably within the range of 50-800.

20      The turbulent stirring during the precipitation phase of the polystyrene allows a finely subdivided precipitate to be obtained, avoiding the formation of gel and minimizing the inclusion of solvent and additives in the precipitate.

25      The polystyrene precipitate is separated by means of a physical method, such as decanting, centrifugation or fil-

tration. This operation is carried out at a temperature ranging from 10°C to 70°C, preferably within the range of 15°C to 60°C.

In order to further reduce the content of additives 5 and solvent (dialkyl carbonate) in the precipitate, the solid is washed using a non-solvent (or blend of non-solvents), preferably the non-solvent (or blend of non-solvents) used in the precipitation.

The washing is carried out at a temperature ranging 10 from 10°C to 80°C, preferably within the range of 15°C to 70°C, by pouring the non-solvent (or blend of non-solvents) onto the filter containing the solid; or by suspending the solid in the non-solvent (or blend of non-solvents), leaving the suspension under stirring, for example for a time 15 ranging from 0.1 to 24 hours and separating the solid by decanting, centrifugation or filtration; or with an extraction in continuous using an extractor, for example of the Soxhlet type. The quantity of non-solvent (or blend of non-solvents) used for the washing ranges from 1 litre to 30 litres per Kg of solid product, preferably within the range 20 of 3 litres to 20 litres per Kg of solid product.

The polymer is dried at a temperature ranging from 50°C to 180°C, preferably within the range of 80°C to 150°C, and at a pressure ranging from 760 mm Hg to 1 mm Hg, 25 preferably within the range of 500 mm Hg to 10 mm Hg.

The dried polymer is extruded with common extruders.

For the separation and recovery of the solvent (dialkyl carbonate), non-solvent and additives, the liquid coming from the filtration of polystyrene and the washing liquid are subjected to distillation using the conventional techniques. The additives remaining as distillation residue can be recovered.

The method described allows the recovery of polystyrene without altering its properties, as it enables the un-  
10 desired additives to be separated from the polymer.

The following examples are provided for illustrative and non-limiting purposes of the present invention.

#### **Examples 1-18**

In these examples, the solubilization capacity of expanded polystyrene on the part of different dialkyl carbonates, was evaluated. This solvent capacity was compared with that of solvents whose use is described in the known art.

A cube of expanded polystyrene having a volume equal  
20 to 125 cm<sup>3</sup> (length = 5 cm, width = 5 cm, depth = 5 cm) is immersed in a glass containing 20 ml of solvent, at room temperature, and the time necessary for completely dissolving the polystyrene is measured. The results of these tests are indicated in Table 1.

Table 1

| Example    | Solvent                         | Solubilization time (seconds) |
|------------|---------------------------------|-------------------------------|
| Ex. 1      | di-methyl carbonate             | 45                            |
| Ex.2       | methyl-ethyl carbonate          | 65                            |
| Ex.3       | di-ethyl carbonate              | 110                           |
| Ex.4       | methyl-isopropyl carbonate      | 115                           |
| Ex.5       | methyl-iso-butyl carbonate      | 140                           |
| Ex.6       | di-n-propyl carbonate           | 180                           |
| Ex.7       | methyl-iso-amyl carbonate       | 190                           |
| Ex.8       | di-n-butyl carbonate            | 290                           |
| Ex.9       | di-iso-amyl carbonate           | 1200                          |
| Ex.10      | butyl-iso-octyl carbonate       | 1980                          |
| Comp.ex.11 | methylene chloride              | 30                            |
| Comp.ex.12 | ethyl acetate                   | 35                            |
| Comp.ex.13 | toluene                         | 45                            |
| Comp.ex.14 | butyl acetate                   | 60                            |
| Comp.ex.15 | diethylene glycol dimethylether | 165                           |
| Comp.ex.16 | limonene                        | 290                           |
| Comp.ex.17 | dimethyl succinate              | 440                           |
| Comp.ex.18 | dimethyl adipate                | 580                           |

As is clearly indicated in Table 1, the dialkyl carbonates (Examples 1-10) generally have a good capacity for dissolving expanded polystyrene. This capacity decreases, in the series of dialkyl carbonates, with an increase in the number of carbon atoms in the alkyl chains. Low-boiling dialkyl carbonates, such as for example dimethyl carbonate (Example 1) (flash point = 17°C) and methyl-ethyl carbonate (Example 2) have a capacity of dissolving polystyrene similar to that of the best solvents in the known art, such as methylene chloride (Comparative example 11), which is suspected to be cancerous; ethyl acetate (Comparative example

12), which has a lower flash point (-4°C); butyl acetate (Comparative example 14), which has a greater toxicity and eco-toxicity; toluene (Comparative example 13), which is harmful. High boiling dialkyl carbonates and with a higher 5 flash point (over 55°C), such as for example di-n-propyl carbonate (Example 6) and dibutyl carbonate (Example 8) have a solvent capacity with respect to polystyrene which is greater than that of alkyl diesters of dicarboxylic acids, such as dimethyl succinate (Comparative example 17) 10 and dimethyl adipate (Comparative example 18) and similar to that of limonene (Comparative example 16) and diethyleneglycol dimethylether (Comparative example 15), which is toxic.

**Example 19****15 Preparation of the polystyrene solution**

210 g of di-n-butyl carbonate are charged into a glass container having a volume of 0.5 litres, equipped with a blade stirrer, thermometer, bottom discharge outlet and inlet for the addition of material. 90 g of expanded poly- 20 styrene reduced to pieces are added in portions to the di-n-butyl carbonate, maintained under stirring at room temperature, and the mixture is left under stirring until complete dissolution. The solution obtained, containing 30% by weight of polystyrene, is filtered in order to eliminate 25 insoluble foreign substances.

The expanded polystyrene used in this and in the subsequent examples is of the flame-retardant type, characterized by a weight average molecular weight equal to 188,000, a bromine content equal to 0.51% by weight and a content of 5 dicumyl peroxide equal to 0.16% by weight.

**Example 20**

**Precipitation and recovery of the polystyrene**

The equipment used for the precipitation of the polystyrene consists of a jacketed glass reactor, having a volume of 1 litre, equipped with a water condenser, thermometer, bottom discharge outlet, Ultra-Turrax stirrer-homogenizer and a feeding plunged piped, having such a form and dimensions that the polystyrene solution is fed below to the stirring system.

15        350 g of n-butanol maintained at a temperature of about 25°C by the circulation of tap water in the reactor jacket, are charged into the reactor described above. The stirring is activated (4,000 revs/minute) and 50 g of the polystyrene solution (30% by weight in di-n-butyl carbon-  
20 ate), prepared in example 19, are fed from the plunged pipe, by means of a gear pump, with a flow-rate of 100 g/hour.

During this phase, the polystyrene precipitates. At the end of the feeding of polymer solution, the solid 25 formed is filtered. The filtered liquid, having a weight of

381 g, has the following composition:

8.4% by weight of di-n-butyl carbonate, 91.6% by weight of butanol, 98 mg/kg of bromine and 55 mg/kg of dicumyl peroxide.

5       The solid on the filter is washed, at room temperature, with 100 g of butanol. The washing liquid, having a weight of 102.2 g, has the following composition:

1.65% by weight of dibutyl carbonate, 98.35% by weight of butanol, 98 mg/kg of bromine and 9.8 mg/kg of dicumyl per-

10      oxide.

The filtration liquid and the washing liquid are distilled in order to recover the butanol and dibutyl carbonate. The bromine and dicumyl peroxide remain in the distillation bottom.

15       The solid on the filter, having a weight of 16.7 g has the following composition:

89% by weight of polystyrene, 3% by weight of butanol, 7.8% by weight of dibutyl carbonate, 0.18% by weight of bromine and 0.012% by weight of dicumyl peroxide.

20       The solid, after drying in an oven for a period of 8 hours at a temperature of 140°C and a pressure of about 50 mm Hg, has a weight of 14.9 g and the following composition:

25       99.8% by weight of polystyrene, 0.02% by weight of dibutyl carbonate, 0.2% by weight of bromine, and 0.013% by weight

of dicumyl peroxide.

The content of bromine and dicumyl peroxide in the polystyrene recovered were reduced by 61% and 92% respectively with respect to the starting expanded polystyrene.

5       The polystyrene recovered is white and has a weight average molecular weight, determined by means of GPC, the same as that of the starting polystyrene.

**Example 21**

10      350 g of n-butanol are charged into the reactor described in example 3, and are maintained at a temperature of about 55°C by circulation of ethylene glycol in the reactor jacket, heated by a thermostatic bath. The stirring is activated (4000 revs/min) and 50 g of the polystyrene solution (30% by weight in di-n-butyl carbonate) prepared  
15     in example 19, are fed from the plunged pipe by means of a gear pump with a flow-rate of 100 g/hour.

20      During this phase, the polystyrene precipitates. Once the feeding of the polymer solution has been completed, the solid formed is decanted and the liquid is separated by suction with a vacuum membrane pump, through a flexible Teflon tube, equipped at one end with a filtration septum. The liquid separated, having a weight of 347.4 g, has the following composition:

25      7.2% by weight of di-n-butyl carbonate, 92.8% by weight of butanol, 127 mg/Kg of bromine and 52 mg/Kg of dicumyl per-

oxide.

The solid remaining in the reactor, having a weight of 52.5 g, has the following composition:

28.4% by weight of polystyrene, 52.2% by weight of butanol,

5 19.4% by weight of dibutyl carbonate, 62.5 mg/Kg of bromine and 115 mg/Kg of dicumyl peroxide.

The solid is washed in the reactor by suspending it in 200 g of n-butanol and leaving the suspension under stirring (4000 revs/min) at room temperature for 45 minutes. At the 10 end of the washing operation the solid is filtered. The washing liquid, having a weight of 234 g, has the following composition:

3.8% by weight of dibutyl carbonate, 96.2% by weight of butanol, 85 mg/Kg of bromine and 23 mg/Kg of dicumyl peroxide.

The filtration liquid and the washing liquid are distilled in order to recover butanol and dibutyl carbonate. Bromine and dicumyl peroxide remain in the distillation bottom.

The solid product on the filter, having a weight of 18.5 g, 20 has the following composition:

80.5% by weight of polystyrene, 12.4% by weight of butanol, 7% by weight of dibutyl carbonate, 690 mg/Kg of bromine and 42 mg/Kg of dicumyl peroxide.

The solid, after drying in an oven for 2 hours at a temperature of 140°C and a pressure of about 50 mmHg, has a

weight of 15 g and the following composition:

99.75% by weight of polystyrene, 0.1% by weight of dibutyl carbonate, 0.04% by weight of butanol, 860 mg/Kg of bromine and 51 mg/Kg of dicumyl peroxide.

5 The content of bromine and dicumyl peroxide in the recovered polystyrene were reduced by 83.2% and 96.8%, respectively, with respect to the starting expanded polystyrene. The recovered polystyrene is white and has a weight average molecular weight, determined by GPC, equal to that of the  
10 starting polystyrene.

#### **Example 22**

210 g of n-butanol and 210 g of propylene carbonate, are charged into the reactor described in example 3 and are maintained at a temperature of about 25°C by circulation of  
15 tap water in the reactor jacket. The stirring is activated (4000 revs/minute) and 70 g of the polystyrene solution (30% by weight in di-n-butyl carbonate), prepared in example 19, are fed from the plunged pipe, by means of a gear pump, with a flow-rate of 100 g/hour.

20 During this phase, the polystyrene precipitates. Once the feeding of the polymer solution has been completed, the solid formed is decanted and the liquid is separated by suction with a vacuum membrane pump, through a flexible Teflon tube, equipped at one end with a filtration septum.  
25 The liquid separated, having a weight of 430.4 g, has the

following composition:

10.2% by weight of di-n-butyl carbonate, 45.2% by weight of butanol, 44.6% by weight of propylene carbonate, 216 mg/Kg of bromine and 69 mg/Kg of dicumyl peroxide.

5 The solid remaining in the reactor, having a weight of 59.6 g, has the following composition:

35% by weight of polystyrene, 25.7% by weight of butanol, 30.3% by weight of propylene carbonate, 8.9% by weight of dibutyl carbonate, 230 mg/Kg of bromine and 70 mg/Kg of di-

10 cumyl peroxide.

The solid is washed in the reactor by suspending it in 200 g of n-butanol and leaving the suspension under stirring (4000 revs/min) at room temperature for 45 minutes. At the end of the washing operation the solid is filtered. The 15 washing liquid, having a weight of 233.6 g, has the following composition:

2.1% by weight of dibutyl carbonate, 91% by weight of butanol, 6.9% by weight of propylene carbonate, 34 mg/Kg of bromine and 15 mg/Kg of dicumyl peroxide.

20 The filtration liquid and the washing liquid are distilled in order to recover butanol and dibutyl carbonate. Bromine and dicumyl peroxide remain in the distillation bottom.

The solid product on the filter, having a weight of 26 g, has the following composition:

25 80.2% by weight of polystyrene, 10.7% by weight of butanol,

7.3% by weight of propylene carbonate, 1.8% by weight of dibutyl carbonate, 240 mg/Kg of bromine and 22 mg/Kg of dicumyl peroxide.

The solid, after drying in an oven for 2 hours at a temperature of 140°C and a pressure of about 50 mmHg, has a weight of 20.9 g and the following composition:

99.85% by weight of polystyrene, 0.05% by weight of dibutyl carbonate, 0.04% by weight of propylene carbonate, 0.01% by weight of butanol, 290 mg/Kg of bromine and 28 mg/Kg of dicumyl peroxide.

The content of bromine and dicumyl peroxide in the recovered polystyrene were reduced by 94.1% and 98.3%, respectively, with respect to the starting expanded polystyrene.

The recovered polystyrene has a weight average molecular weight, determined by GPC, equal to that of the starting polystyrene.